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A bio-inspired molecular catalyst that selectively catalyzes water oxidation in seawater, without significant chlorine formation

Abstract

Most transport fuels are derived from fossil fuels, generate greenhouse gases, and consume significant amounts of water in the extraction, purification, and/or burning processes. The generation of hydrogen using solar energy to split water, ideally from sea water or other non-potable sources, could potentially provide an unlimited, clean fuel for the future. Solar, electrochemical water splitting typically combines a photoanode at which water oxidation occurs, with a cathode for proton reduction to hydrogen. In recent work we have found that a bioinspired tetra-manganese cluster catalyzes water oxidation at relatively low overpotentials (0.38 V) when doped into a Nafion proton conduction membrane deposited on a suitable electrode surface, and illuminated with visible light. We report here that this assembly is active in electrolyte solutions containing a range of different salts in varying concentrations. Similar photocurrents were obtained using sodium sulfate, sodium perchlorate, or sodium chloride over various electrolyte concentrations (0.0 - 0.5 M). The photocurrent declined only at and above 5.0 M sodium perchlorate. Remarkably, the photocurrent did not increase in the presence of chloride ions, either in saturated aqueous NaCl or in non-aqueous acetonitrile. Moreover, testing of the system in sea water generated the same photocurrent as aqueous 0.1 M Na₂SO₄. In a normal water electrolysis cell, chlorine gas would be preferentially formed from chloride (before water oxidation) because, while the standard potential of water oxidation is lower than that of chloride, its overpotential is substantially higher. The catalyst-induced decline in overpotential and, possibly, the impermeability of Nafion to chloride ions, reverses this situation in the present system. This finding raises the possibility of developing a novel, solar-powered desalination process.

Keywords

catalyst, that, selectively, catalyzes, inspired, bio, without, seawater, formation, chlorine, significant, oxidation, water, molecular

Disciplines

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A bio-inspired molecular catalyst that selectively catalyzes water oxidation in seawater, without significant chlorine formation

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ABSTRACT

Most transport fuels are derived from fossil fuels, generate greenhouse gases, and consume significant amounts of water in the extraction, purification, and/or burning processes. The generation of hydrogen using solar energy to split water, ideally from sea water or other non-potable sources, could potentially provide an unlimited, clean fuel for the future. Solar, electrochemical water splitting typically combines a photoanode at which water oxidation occurs, with a cathode for proton reduction to hydrogen. In recent work we have found that a bioinspired tetra-manganese cluster catalyzes water oxidation at relatively low overpotentials (0.38 V) when doped into a Nafion proton conduction membrane deposited on a suitable electrode surface, and illuminated with visible light. We report here that this assembly is active in electrolyte solutions containing a range of different salts in varying concentrations. Similar photocurrents were obtained using sodium sulfate, sodium perchlorate, or sodium chloride over various electrolyte concentrations (0.0 - 0.5 M). The photocurrent declined only at and above 5.0 M sodium perchlorate. Remarkably, the photocurrent did not increase in the presence of chloride ions, either in saturated aqueous NaCl or in non-aqueous acetonitrile. Moreover, testing of the system in sea water generated the same photocurrent as aqueous 0.1 M Na₂SO₄. In a normal water electrolysis cell, chlorine gas would be preferentially formed from chloride (before water oxidation) because, while the standard potential of water oxidation is lower than that of chloride, its overpotential is substantially higher. The catalyst-induced decline in overpotential and, possibly, the impermeability of Nafion to chloride ions, reverses this situation in the present system. This finding raises the possibility of developing a novel, solar-powered desalination process.

Keywords: Water oxidation, PSII, salt effects, sea water, hydrogen, photocatalysis

INTRODUCTION

Recent developments in renewable energy technologies, such as wind, photovoltaic, geothermal, tidal and wave, have seen a significant increase in the production of clean electricity. However, the challenges of producing low-carbon, renewable, transport fuels remains. Hydrogen is a carbon-free, high-energy carrier that can be utilized efficiently in a range of applications. It remains one of the most promising fuels of the future. [1, 2]

Hydrogen can be produced using a variety of techniques and from a range of feedstocks. However, many of these rely on fossil fuels and the subsequent release of carbon dioxide into the atmosphere (for example, steam reforming from natural gas).[1] An ideal source of hydrogen gas is through the splitting of water using renewable energy sources ($2\text{H}_2\text{O} \rightarrow \text{O}_2 + 2\text{H}_2$). This can be achieved by water electrolyzers that combine a water oxidation anode with a cathode for proton reduction. Of these two processes, the oxidation of water is thermodynamically very demanding:

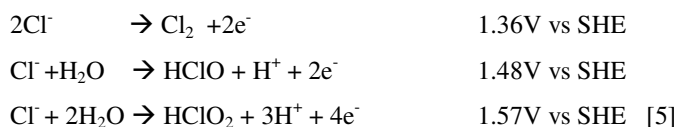


The theoretical potential required to drive water oxidation falls to 0.82 V at pH 7. In practice, however, mechanistic complexity coupled with a substantial activation barrier means that a large electrochemical overpotential is needed to drive this reaction. Typical water electrolyzers therefore operate at ca. 2 V. For water splitting using renewable energy to be successful, catalysts are needed to lower the overpotential and, therefore also the overall voltage required to achieve water oxidation.

A further major challenge in developing a sustainable supply of hydrogen is the source of water for electrolysis. Water is an essential part of human life and is becoming an increasingly precious resource. The extraction, production, and delivery of most transport fuels require a significant amount of water. The total water (consumed and used in cooling cycles, washing etc.) required to travel one mile in a typical car using gasoline/petroleum has been calculated to be ca. 0.63 gallons $\text{H}_2\text{O}/\text{mile}$, with a gallon of gasoline requiring approximately 12.5 gallons of water to produce.[3] Hydrogen from natural gas steam reforming equates to approximately 0.07 gallons $\text{H}_2\text{O}/\text{mile}$. Hydrogen produced from coal powered electricity using conventional electrolysis technology has a water intensity of 13 gallons $\text{H}_2\text{O}/\text{mile}$, due to the large amount of water utilized (primarily for cooling) in coal power stations. Electrolysis using a renewable energy source such as wind or solar, has a much lower water intensity of 0.03 gallons $\text{H}_2\text{O}/\text{mile}$. Thus, the production of hydrogen via electrolysis using renewable energy would have a favorable impact on the amount of water consumed compared to most other transport fuels.

For most electrolyzers and catalytic systems the water feedstock needs to be quite pure to prevent corrosion.[1] If we assume that the water used must be of be quality similar to drinking water, then meeting the transport fuel demand of hydrogen would require a significant investment of clean water given the large number of commuter miles traveled each day. Thus, the challenge for sustainably producing hydrogen from water is not only to develop catalysts to reduce the energy requirement but also to design a catalytic system that is able to produce hydrogen from non-potable sources.

Sea water is one of the most abundant, accessible resources on Earth. It contains a range of inorganic ions, organic molecules and biological material, with the concentration of these components varying widely around the world. Typical sea water contains common ions, including Cl^- , Na^+ , Mg^{2+} , SO_4^{2-} , Ca^{2+} , K^+ and HCO_3^- , listed in order of decreasing concentration. Of these ions, Cl^- and Na^+ are the most abundant, with a standard mean chemical concentration of 0.55 M and 0.47 M, respectively.[4] In non-catalyzed electrolysis devices, the use of conducting electrolytes like aqueous sodium chloride (sea water), is typically not appropriate due to the range of oxidation processes that aqueous chloride ions may undergo at the potentials applied.[5] These include:



In a standard electrolysis cell operating at around 2 V, chloride oxidation processes would readily occur at the anode and would occur preferentially. These processes would reduce the efficiency of the cell, consuming a significant portion of the applied energy and generate undesirable by-products such as Cl_2 , which is a highly reactive (oxidizing) and toxic gas. For efficient electrolysis of sea water, a catalyst is therefore required that selectively lowers the actual potential of water oxidation to below that of chloride. The majority of catalysts used in efficient commercially available water electrolysis devices are solid films of noble metals such as Pt, Ir and Ru, with Pt the most commonly used.[6, 7] These materials also catalyze chloride oxidation, which has a small overpotential; that is, chloride is oxidized in preference to water in sea water at the operating potential of water electrolysis devices. This is also true for non-specific metal oxide catalysts, limiting their application as catalysts for oxidation of sea water.

The most efficient known system for harnessing solar energy to oxidize water is the Photosystem II (PSII) complex that makes up part of the photosynthetic apparatus found in plants. At the core of Photosystem II is a tetra-manganese cluster referred to as the water oxidation complex (PSII-WOC).[8, 9] This cluster achieves efficient oxidation of water and is highly specific for water molecules. It is protected within a membrane bound protein active site that tightly controls the concentration of ions such as Cl^- . This specificity has allowed photosynthetic organisms to flourish wherever there is a source of water, including in the oceans. The oxidation process is achieved with a driving potential (provided by the light absorbing pigments) of 1.25 V vs SHE.[10]

We previously described a method for inducing a bio-inspired manganese cubane cluster $[\text{Mn}_4\text{O}_4\text{L}_6]^+$ ($\text{L} = (p\text{-MeO-Ph})_2\text{PO}_2$) [11, 12] to undertake catalytic water oxidation when supported in a proton-conducting membrane, Nafion. [13] Investigation of the mechanism of catalysis suggests that water oxidation is achieved via an intra-molecular process where two of the core oxo ligands form a di-oxygen bond resulting in the evolution of O_2 , followed by the binding of water, which facilitates the regeneration of the cubane core upon the release of protons.[14] This process takes place at the hydrophobic/hydrophilic interface found within the channels of the Nafion membrane when it is cast as a thin layer upon a conducting electrode. The channels of Nafion are proton conductors and are selectively permeable to cations (and not anions) due to the lining of sulfonate anions (Figure 1).[15] In addition to providing an interface for the cluster to interact with water and the electrode, and for protecting the cluster from the bulk water solution, the Nafion sulfonate groups are thought to assist in the removal of protons arising from water in the catalytic process.[14]

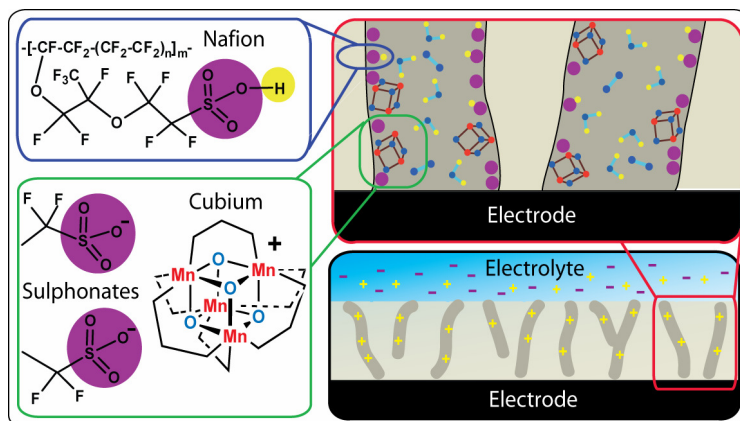


Fig. 1. Schematic representation of the catalytic manganese cubium, $[\text{Mn}_4\text{O}_4\text{L}_6]^+$ ($\text{L} = (p\text{-MeO-Ph})_2\text{PO}_2$), suspended in a Nafion membrane. Figure adapted from Brimblecombe *et al.* 2009.[14]

In the current study, we have investigated the influence of varying concentrations of three different electrolytes, sodium sulfate, sodium perchlorate and sodium chloride, on the catalytic activity of the cubium, $[\text{Mn}_4\text{O}_4\text{L}_6]^+$ /Nafion catalyst. The selectivity of this catalytic system to preferentially oxidize water in solutions containing typical sea water NaCl concentrations was also examined. Finally the activity of the system was tested in a sample of sea water.

1. EXPERIMENTAL SECTION

Materials and Methods: Bis(methoxyphenyl)phosphinic acid was purchased from Aldrich, and used without further purification. Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) was obtained from GFS Chemicals and purified by a published procedure.[16] Nafion[®] was purchased from Dupont as a Nafion - PFSA polymer dispersion DE 1020, which is an aqueous dispersion of 10-12% Nafion. All other reagents were purchased from BDH or Aldrich and used as received. Cubane $[\text{Mn}_4\text{O}_4\text{L}_6]$, (L = bis(p-methoxyphenyl)phosphinate) and cubium $[\text{Mn}_4\text{O}_4\text{L}_6]^+\text{ClO}_4^-$ were prepared as described in literature.[17]

Electrochemistry: Electrochemical experiments were conducted at $22(\pm 2)^\circ\text{C}$ with BAS (Bio Analytical Systems) Epsilon CS3 or BAS 100B workstations. Cyclic voltammograms were obtained at scan rates of 5 to 500 mVs^{-1} in a conventional three electrode electrochemical cell containing inlet and outlet ports for degassing solutions with nitrogen. Experiments in CH_2Cl_2 or CH_3CN (0.1 M Bu_4NPF_6), used an Ag/Ag^+ (0.01 M AgNO_3 in CH_3CN) reference electrode, with a double glass frit separating the electrode from the test solution. The ferrocene/ferrocenium oxidation process was used to provide an internal reference potential calibration system for electrochemical studies in organic solvents (0.400 V vs NHE at 25°C [5]). Aqueous experiments were conducted in distilled water containing 0.1 M Na_2SO_4 as the electrolyte. In this case, potentials were referenced against a BAS Ag/AgCl (3 M NaCl) glass bodied reference electrode separated from the test solution by a Vycor frit, with a potential of 0.200 V vs NHE at 25°C (BAS reference electrode users manual). All voltammetric experiments used Pt wire or a Pt mesh auxiliary electrodes.

The working electrodes used were 3 mm diameter glassy carbon and Pt disc electrodes. The glassy carbon working electrode had an electroactive area of 5.9 mm^2 as determined by oxidation of 1.0 mM ferrocene in CH_3CN (0.5 M Bu_4NPF_6) and use of the Randles-Sevcik equation [5] with a diffusion coefficient (D) of $1.7 \times 10^{-5}\text{ cm}^2\text{s}^{-1}$.

Film Deposition and Nafion Doping: Nafion modified electrodes were prepared by drop-casting a suspension of 10% Nafion onto the working electrode and heating in a laboratory oven at 120°C for 20 min. Doping of the cast Nafion membrane was achieved by immersion in a 2 mM CH_3CN solution of $[\text{Mn}_4\text{O}_4\text{L}_6]^+\text{ClO}_4^-$. Cubium in Nafion is reduced to cubane, at the initial potential used in cyclic voltammetry.

Light Source: The Xenon light source used for these experiments generated white light with a stable output over the range 250-750 nm, from a Rofin Australia-Polilight PL6, passed through a 1 m long liquid light guide. Illumination experiments were conducted at a light intensity of approximately $500\text{ mW}/\text{cm}^2$, measured at the electrode surface.

Salt Concentration Film Testing: The working, reference and counter electrodes were fixed together in a standard configuration and moved between the testing electrolytes as one unit, with rinsing on transfer between individual electrolyte preparations, using the respective solvents. Aqueous electrolytes were prepared by dissolving Na_2SO_4 , NaClO_4 or NaCl in unbuffered distilled water (pH 6.7). Sea water samples were collected from Port Phillip Bay, Melbourne Australia, and filtered using filter paper to remove particulates. The samples had a pH of 6.9. Photocurrent was investigated for the aqueous electrolyte at 1.00 V vs an Ag/AgCl reference electrode. All acetonitrile solutions contained 0.1 M Bu_4NPF_6 . Distilled water was added to the acetonitrile 0.1 M Bu_4NPF_6 electrolyte to achieve a 10% (v/v) solution. $\text{Bu}_4\text{NCl}\cdot\text{H}_2\text{O}$ was added to the acetonitrile 0.1 M Bu_4NPF_6 electrolyte to a concentration of 0.1 M.

2. RESULTS AND DISCUSSION

2.1 Ionic strength and Photocurrent

We previously reported that a consistent photocurrent was observed for the cubium/Nafion system using a range of electrode materials, including Pt, glassy carbon and ITO, and in a range electrolytes at 0.1 M, including Na_2SO_4 , NaF, Bu_4NPF_6 , Bu_4NClO_4 . [18] To further investigate the effect of electrolyte, catalytic testing has now been undertaken using Na_2SO_4 and NaCl (0 M – saturation), as well as NaClO_4 (0 – 5 M).

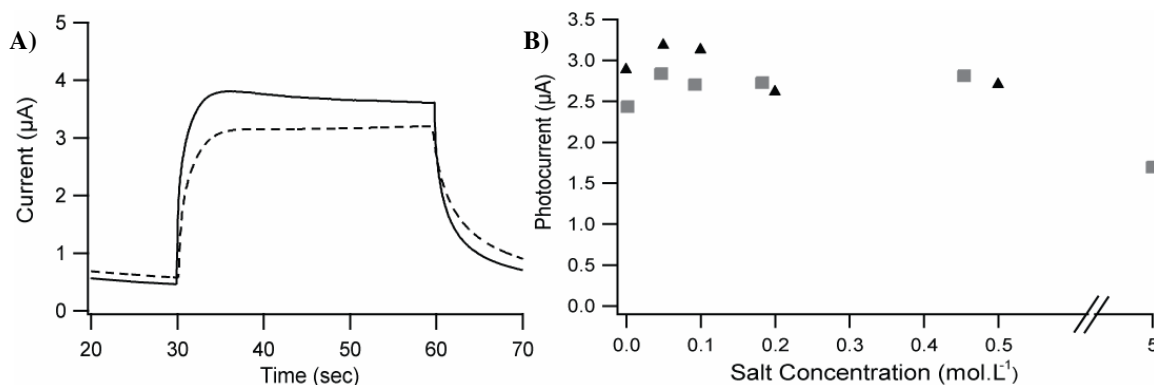


Fig. 2. A) Photocurrent of cubane/Nafion-GCE in illuminated at 1V (vs Ag/AgCl) in neat water (-----), and saturated aqueous Na₂SO₄ (——). B) Plot of photocurrent with increasing Na₂SO₄ (▲) and NaClO₄ (■) concentration.

The first series of experiments were conducted using sodium sulfate and sodium perchlorate electrolyte. As depicted in Fig. 2A, increasing the concentrations of these electrolytes had no significant effect on photocurrent for concentrations up to 0.5 M. A slight decrease in photocurrent was observed when the concentration of NaClO₄ was raised to 5 M. We have previously demonstrated using cyclic voltammetry, that electrochemical conductivity is improved by the presence of protons.[16] This may be due to the ability of the cluster to migrate to the electrode surface to liberate electrons. During water oxidation, conductivity is maintained by the protons generated by the oxidation process, thereby enabling a photocurrent to be sustained over the short time scale displayed in Fig. 2. We also previously demonstrated that photocurrent increases with increasing pH which is expected from the relationship between water oxidation and proton concentration, with the potential required to oxidize water becoming 59 mV more positive for evener decrease in pH unit. From the current investigation, we conclude the salt concentration has no observable affect on photocurrent at concentration lower than 1M and only a small negative effect at very high salt concentrations.

2.2 Catalytic selectivity

The cubium/Nafion catalytic assembly has been shown to produce minimal (background) photocurrent when immersed in acetonitrile.[14, 18] As increasing concentrations of water were titrated into the acetonitrile electrolyte the magnitude of the photocurrent progressively increased, flattening out at approximately 8% water (v/v). This demonstrates that the magnitude of the photocurrent is proportional to the concentration of oxidizable substrate at the cluster active sites within the membrane. The cubanes are also able to oxidize simple organic molecules, such as thioethers, hydrocarbons, alkenes, benzyol alcohol and benzaldehyde, when dissolved in organic solution.[19] This led us to examine whether the cubium/Nafion catalytic system is able to oxidize benzyol alcohol when present in an aqueous solution. As shown in Fig. 3, photocurrent dramatically increases on the addition of benzyol alcohol to the aqueous electrolyte. The oxidation of organic molecules like benzyol alcohol, is energetically less demanding than the oxidation of water. From this we conclude that the photocurrent is dependent on the rate at which the cubium/Nafion system is able to catalyze the oxidation of individual substrates.

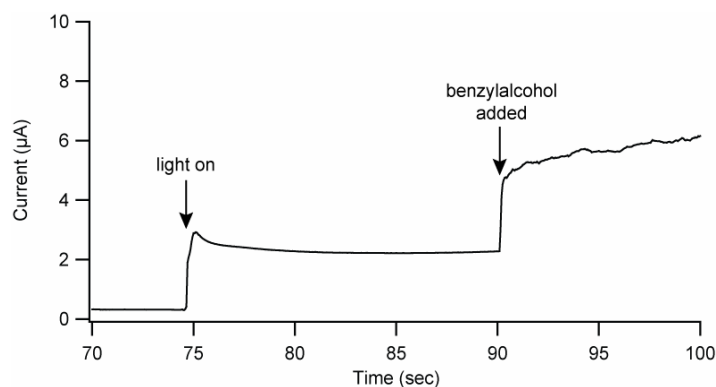


Figure 3. Photocurrent of the cubium/Nafion-GCE in 0.1M Na₂SO₄ aqueous solution at 1V, before and after the addition of benzyl alcohol.

For the cubium/Nafion system to utilize water sources like sea water, the system must be able to preferentially catalyze the oxidation of water rather than chloride ions, typically present at concentrations of ~0.5 M. As shown in Fig.4 (Fig. 4A), the Cl⁻ oxidation processes at a Nafion coated glassy carbon electrode are observed over the potential range of 1.2-1.4 V (vs Ag/AgCl), with the oxidation of the bulk water solution occurring at more positive potentials >1.5 V.

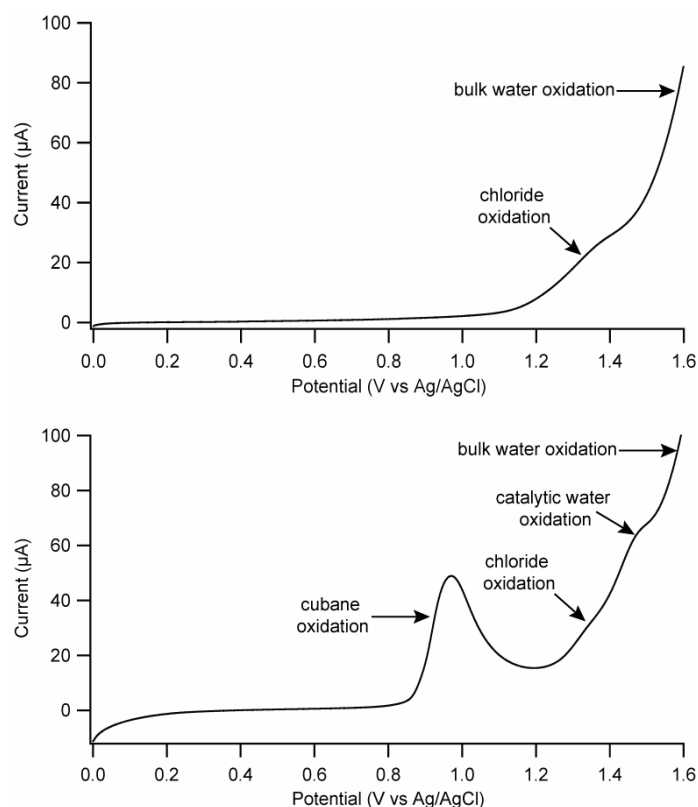


Fig. 4. Linear sweep voltammetry in aqueous 0.1 M Na₂SO₄, 0.05 M NaCl at a scan rate of 10 mVs⁻¹ of a: A) Nafion coated glassy carbon electrode (top trace), B) Nafion doped with manganese cubane on a glassy carbon electrode (bottom trace).

Previous investigation of the cubium/Nafion system suggests that a potential is required to generate the oxidized cubium state of the manganese cluster. Upon illumination the cubium is thought to evolve oxygen generating a $\{\text{Mn}_4\text{O}_2\}$ core. The reduced cluster binds water molecules and is re-oxidized by the external potential releasing four protons and regenerating the cubium state.[14] Thus, the applied potential is required only to oxidize the manganese cluster which, in turn, is able to oxidize water and evolve O_2 . The applied potential (1.00 V vs Ag/AgCl) is significantly less positive than the potential required to oxidize water at the Nafion coated electrode (Fig. 2A). Thus, all water oxidation is thought to occur via the manganese cluster. The oxidation potential of manganese cubane to the cubium state ($[\text{Mn}_4\text{O}_4\text{L}_6]^+$) is observed in Fig. 4B at approximately 0.95 V, 300 mV below the observed oxidation wave of Cl^- (1.25-1.4 V). As shown in Fig. 4A, in aqueous solution, chloride ions are not oxidized at the Nafion coated electrode at potentials of 1.00 V (vs Ag/AgCl). Thus, operation of this catalyst should not result in Cl_2 generation at the electrode surface unless the electrode surface can also catalyze the oxidation of Cl^- .

As shown in Fig. 5A, no increase in photocurrent was observed even when saturated NaCl was used as the electrolyte. As the photocurrent clearly increased in the presence of benzyl alcohol, if the cubium/Nafion system was able to catalyze the oxidation of Cl^- the photocurrent would be expected to increase with increasing Cl^- concentration in the electrolyte. The fact that such an increase was not observed even in a saturated brine solution suggests that the cubium does not catalyze the oxidation of Cl^- in aqueous solutions or at least preferentially oxidizes water in the presence of Cl^- ions. To further investigate the ability of the cubium to catalyze the oxidation of Cl^- , we immersed the cubium/Nafion system in a solution of acetonitrile (0.1 M Bu_4NPF_6) containing Bu_4NCl .

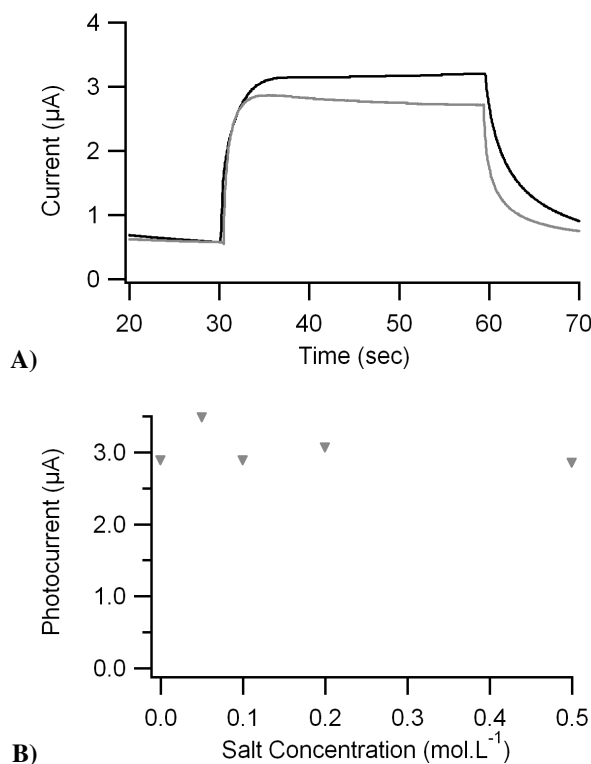


Fig. 5. A) Photocurrent of cubane/Nafion-GCE in illuminated at 1.00 V (vs Ag/AgCl) in neat water (grey line), saturated aqueous NaCl (black line). B) Plot of photocurrent with increasing NaCl (\blacktriangledown) concentration.

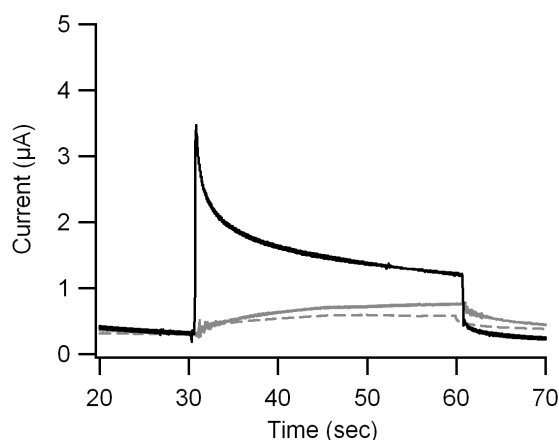


Fig. 6. Photocurrent from a cubium/Nafion Glassy carbon electrode, poised at the oxidation potential of the cubane, in acetonitrile 0.1 M Bu_4NPF_6 (-----), in acetonitrile with $\text{Bu}_4\text{NCl.H}_2\text{O}$ (grey line) and in acetonitrile with 10% (v/v) water (black line).

As displayed in Fig. 6 the addition of Bu_4NCl does not result in a significant photocurrent above that observed for Bu_4NPF_6 , while the addition of water dramatically increases the observed photocurrent. The very slight increase in photocurrent of Bu_4NCl over Bu_4NPF_6 is most likely due to the small amount of water in the salts and/or solvent. In addition, the increase in dark current following illumination suggests that heating of the electrode (during illumination) may facilitate a small amount of background chloride oxidation at the glassy carbon electrode, which was observed by cyclic voltammetry to be as little as 100 mV more positive than the potential required to oxidize cubane to cubium in Nafion. As no significant photocurrent was observed in the presence of chloride and no increase in photocurrent was observed in aqueous solutions saturated with NaCl we conclude that the cubium/Nafion system does not catalyze chloride oxidation at the 1.00 V (vs AgCl) potential applied to achieve catalytic water oxidation.

The observed results suggest that the cubium/Nafion system should be able to readily generate protons and electrons using sea water as the water source. To investigate this we tested the system using a sample of sea water as the electrolyte. As shown in Fig. 7 the photocurrent arising from sea water electrolyte was equivalent to photocurrent observed for a solution of 0.1 M Na_2SO_4 .

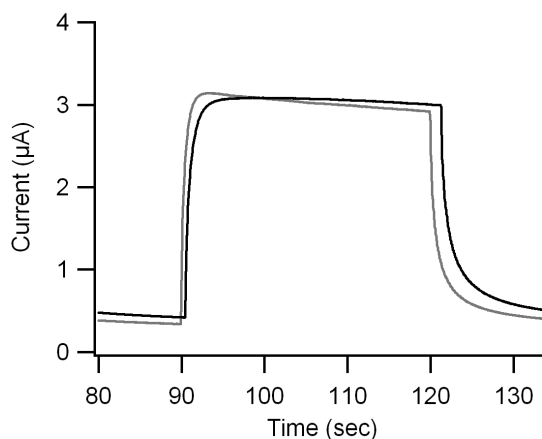


Fig. 7. Photocurrent of cubane/Nafion-GCE in illuminated at 1.00 V (vs Ag/AgCl) in aqueous 0.1 M Na_2SO_4 (grey line) and a sample of sea water (black line).

3. CONCLUSIONS.

The ionic strength of the supporting electrolyte appears to have no significant influence on the ability of the cubium/Nafion system to oxidize water at concentrations of 0.0 - 0.5 M. The oxidation of chloride in aqueous solution at a Nafion coated glassy carbon electrode was found to occur at potentials >300 mV more positive of the potentials required to generate the catalytically active cubium species. The addition of NaCl to the supporting aqueous electrolyte did not result in an increase in photocurrent at 1,00 V (vs AgCl), which would be expected if the cubium/Nafion system catalyzed Cl^- oxidation. Furthermore, in the absence of water, no significant photocurrent was observed with acetonitrile solutions containing chloride, suggesting the cubium/Nafion system is not able to catalyze the oxidation of chloride. This selectivity is likely to result from: (1) the ability of the manganese cubium to oxidize water at potentials significantly less positive than those required to oxidize chloride ions; (2) the specificity of the cubium for water oxidation which could arise from the intra-molecular nature of this process; (3) the cation specificity of the Nafion membrane, which may limit the concentration of chloride ions in the vicinity of the cubium active sites. As the system does not oxidize chloride and is unaffected by ionic concentrations observed in abundant water sources such as sea water, we propose that a range of non-potable water sources could potentially be utilized in the practical operation of this system. These findings raises the possibility of using the cubium/Nafion system in a novel, solar-powered desalination process.

Further studies of the system are underway and will be reported in a full paper.

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